Analytical Method for Mandipropamid (Agricultural Products)

1. Analyte

Mandipropamid

2. Instrument

Liquid chromatograph-mass spectrometer (LC-MS)

3. Reagents

Use the reagents listed in Section 3 of the General Rules, except the following.

Reference standard of mandipropamid: Contains not less than 98% of mandipropamid.

4. Procedure

1) Extraction

For fruits and vegetables, weigh 20.0 g of sample. For grains, legumes, nuts and seeds, weigh 10.0 g of sample, for tea leaves, weigh 5.00 g of sample, add 20 mL of water and let stand for 30 minutes.

Add 100 mL of acetonitrile, homogenize, and filter with suction. Add 50 mL of acetonitrile to the residue on the filter paper, homogenize, and filter with suction. Combine the resulting filtrates, and add acetonitrile to make exactly 200 mL. Take a 2 mL (4 mL for tea leaves) aliquot of the extract, and add 6 mL (12 mL for tea leaves) of water.

2) Clean-up

i) Octadecylsilanized silica gel column chromatography and graphitized carbon black column chromatography

Add 5 mL each of acetonitrile and water to an octadecylsilanized silica gel cartridge (1,000 mg) sequentially, and discard the effluent. Add 5 mL each of acetonitrile and water to a graphitized carbon black cartridge (500 mg) sequentially, and discard the effluent. Transfer the extract obtained in 1) to the octadecylsilanized silica gel cartridge, add 5 mL of acetonitrile/water (1:1, v/v), and discard the effluent. Connect the graphitized carbon black cartridge at the bottom of the octadecylsilanized silica gel cartridge, add 10 mL of acetonitrile/water (7:3, v/v), and discard the effluent. Remove the octadecylsilanized silica gel cartridge, add 10 mL of acetonitrile/water (9:1, v/v) to the graphitized carbon black cartridge, and discard the effluent. Elute with 20 mL of acetone, concentrate the eluate at below 40°C and remove the solvent. Dissolve the residue in 5 mL of ethyl acetate/*n*-hexane (1:4, v/v).

ii) Silica gel column chromatography

Add 5 mL of ethyl acetate/*n*-hexane (1:4, v/v) to a silica gel cartridge (690 mg) and discard the effluent. Transfer the solution obtained in i) to the cartridge, add 5 mL of ethyl acetate/*n*-hexane (1:4, v/v), and discard the effluent. Elute with 10 mL of ethyl

acetate/*n*-hexane (2:3, v/v), concentrate the eluate at below 40°C and remove the solvent. Dissolve the residue in acetonitrile/formic acid/water (500:1:500, v/v/v) to make exactly 4 mL for fruits and vegetables, 2 mL for grains, legumes, nuts and seeds, and tea leaves, and use this solution as the test solution.

5. Calibration curve

Prepare 0.0005–0.01mg/L mandipropamid standard solutions (acetonitrile/formic acid/water (500:1:500, v/v/v)). Inject 10 μL of each standard solution to LC-MS, and make a calibration curve by peak-height or peak-area method.

6. Quantification

Inject 10 μL of the test solution to LC-MS and calculate the concentration of mandipropamid from the calibration curve made in **5**.

7. Confirmation

Confirm using LC-MS.

8. Measurement conditions

Example

Column: Octadecylsilanized silica gel, 2.1 mm in inside diameter, 150 mm in length and 5 μm in particle diameter

Column temperature: 40°C

Mobile phase: acetonitrile/formic acid/water (500:1:500, v/v/v)

Ionization mode: ESI (+)

Major monitoring ions (*m/z*): 414, 412

Expected retention time: 8 min

9. Limit of quantification

0.01 mg/kg

10. Explanatory note

1) Outline of analytical method

The method consists of extraction of mandipropamid from sample with acetonitrile, clean-up with an octadecylsilanized silica gel cartridge, a graphitized carbon black cartridge, and a silica gel cartridge, quantification and confirmation using LC-MS.

2) Notes

i) When the analytical method for mandipropamid using LC-MS was developed, the following monitoring ions were used:

for quantification ion (*m/z*): 412

for confirmation (*m/z*): 414

ii) For agricultural products containing a small amounts of matrix components, clean-up with the graphitized carbon black cartridge can be omitted.

iii) It has been reported that “Multi-residue Method I for Agricultural Chemicals by LC-MS (Agricultural Products)” is applicable to mandipropamid in soybeans, cabbage and grape.

11. References

None

12. Type

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